

Mechanical properties of composites based on unsaturated polyester resins obtained by chemical recycling of poly(ethylene terephthalate)

Aleksandar D. Marinković¹, Tijana Radoman², Enis S. Džunuzović¹, Jasna V. Džunuzović³, Pavle Spasojević¹, Bojana Isailović¹, Branko Bugarski¹

¹Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia

²Innovation center, Faculty of Technology and Metallurgy, University of Belgrade, Belgrade, Serbia

³Institute of Chemistry, Technology and Metallurgy (ICTM) – Center of Chemistry, University of Belgrade, Belgrade, Serbia

Abstract

Composites based on unsaturated polyester (UPe) resins and fumed silica AEROSIL® RY 50, NY 50, RX 50 and NAX 50, as well as graphite, TiO₂ or organically modified clay CLOISITE 30B were prepared in order to investigate the influence of reinforcing agents on the mechanical properties of composites. Unsaturated polyester resins were synthesized from maleic anhydride and products of glycolysis, obtained by depolymerization of poly(ethylene terephthalate) with dipropylene glycol (UPe1 resin) and triethylene glycol (UPe2 resin) in the presence of tetrabutyl titanate catalyst. The obtained unsaturated polyesters were characterized by FTIR spectroscopy, acid and hydroxyl values, and their mechanical properties were also examined. Significant increase of the tensile modulus, tensile strength and decrease of the elongation at break was observed for composites prepared after addition of 10 wt.% of graphite or 10 wt.% of TiO₂ to the UPe resins, indicating strong interaction between matrix and filler particles. On the other hand, nanocomposites prepared using UPe2 and hydrophobically modified silica nanoparticles showed lower tensile strength and tensile modulus than polymer matrix. The presence of CLOISITE 30B had no significant influence on the mechanical properties of UPe1, while tensile strength and tensile modulus of UPe2 increased after adding 10 wt.% of clay.

Keywords: poly(ethylene terephthalate), chemical recycling; composites, mechanical properties.

Available online at the Journal website: <http://www.ache.org.rs/HI/>

Poly(ethylene terephthalate) (PET) is a semi-crystalline, thermoplastic polyester that exhibits very good mechanical properties, good barrier properties and high transparency. Because of this, it is used for the production of packaging materials for soft drinks, food and pharmaceuticals, synthetic textile, photo-paper and for engineering plastics (usually reinforced with glass fibers). The production and consumption of PET products recorded the fastest growth rate in the global plastics market, but the current consumption of plastic containers is generating a huge amount of polymer waste. PET accounts for more than 8 wt.% and 12 vol.% of the world's solid waste generation [1].

The wide application and permanent increase in consumption of PET based products caused unavoidable generation of large volume of PET waste (rapid growing), which created a major environmental problem because PET is very resistant to biodegradation. Increased environmental awareness, legislative mea-

Correspondence: A.D. Marinković, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11120 Belgrade, Serbia.
E-mail: marinko@tmf.bg.ac.rs

Paper received: 30 September, 2013

Paper accepted: 14 October, 2013

Polymers

SCIENTIFIC PAPER

UDC 678.7–19:66.095.26:620.1/.2

Hem. Ind. **67** (6) 913–922 (2013)

doi: 10.2298/HEMIND130930077M

asures and public need for the sustainable development, increased interest in recycling of plastics. Plastic recycling is important from several aspects, such as energy conservation, reduced oil consumption, saving space in landfills, reduced greenhouse gas emissions and the benefits of reuse [1]. Recycling of plastic materials is divided into four categories: primary (re-extrusion), secondary (mechanical), tertiary (chemical) and quaternary (energy recovery – incineration) [2]. Chemical processing of PET and reuse of the obtained products are the most important strategy for PET recycling. PET has ester groups that can degrade using a variety of reagents such as acids, bases or water (hydrolysis of PET) [3,4], alcohols (PET alcoholysis) [5], amines (PET aminolysis) [6], glycols (PET glycolysis) [7–9], etc. In the PET glycolysis process, oligomeric products with terminal hydroxyl groups were obtained by PET depolymerization reaction with different glycol. The resulting oligomers can be used for the synthesis of various polymers, such as alkyd resins [10,11], polyurethanes [12,13] or unsaturated polyester (UPe) resins [14–16].

Unsaturated polyester resins are thermosetting polymers that are widely used in the preparation of polymer composites [17–19]. Extensive use of these materials is a consequence of their relatively low cost,

easy of processing, good compatibility with a variety of fillers, as well as large selection of various types. However, compared with other engineering polymers, unsaturated polyesters have lower mechanical and thermal properties, which limit their use for some applications. These imperfections can be removed by adding various modified fillers [20–23]. Conventional fillers are used to improve the mechanical properties and to reduce the production costs, but their use is limited since they may lead to the phase separation and agglomeration of the filler particles, leading to a drastic deterioration of the material properties [24].

The incorporation of clay into UPe resin can result in improvements of mechanical, thermal, barrier and chemical properties, wear resistance and flame retardancy [25–29]. This can be done with less clay content than what is usually used in most conventional composites.

The most commonly used clay for polymeric composites is montmorillonite (MMT), which belongs to the general family of 2:1 layered silicates [30], and it is consisted of two fused silicate tetrahedral sheets sandwiching an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. Only few works have been reported based on MMT-UPe resin derived from PET waste. Jo *et al.* [31] investigated mechanical properties and thermal stability of MMT-UPe nanocomposites and polymer concrete prepared using the MMT-UPe nanocomposite, and found that the compressive strength, elastic modulus, and splitting tensile strength of the polymer concrete based on MMT-UPe nanocomposites exceeded those of polymer concrete obtained using pure UPe resin. Also, the polymer concrete made with MMT-UPe nanocomposite showed better thermal performance than that made of pure UPe resin. Water sorption and diffusion of the MMT-UPe system was investigated by Katoch *et al.* [32]. The authors concluded that nanocomposite samples show lower diffusion coefficient than pure UPe and it decreases with increasing nanofiller content up to 4% by weight.

In this work, hybrid materials based on UPe matrix and graphite powder (GP), TiO₂, chemically modified clay CLOISITE 30B or chemically modified silica nanoparticles were prepared in order to study the influence of reinforcing agents on the mechanical properties of the obtained composite materials. Unsaturated polyesters were synthesized from di-hydroxyl functional product obtained by different methods of catalytic glycolysis of PET waste, using dipropylene glycol (DPG) and triethylene glycol (TEG), and maleic anhydride.

EXPERIMENTAL PART

Chemicals

Hydroquinone (HQ), dipropylene glycol (DPG) and triethylene glycol (TEG) were obtained from Fluka.

Maleic anhydride (MA) was obtained from Sigma Aldrich. Tetrabutyl titanate (titanium (IV) butoxide; TBT) was obtained from Sigma-Aldrich. As fillers, graphite powder (GP; Dragon) and TiO₂ (Qingdao David Chemical Co., Ltd.) in the rutile crystal form (particle diameter of 0.25 μm and density of 3.9 kg dm⁻³) were used. Four different hydrophobic nanosilica were obtained from Evonik. Aerosil® RY 50 (specific surface area of 30±15 m² g⁻¹) and Aerosil® NY 50 (specific surface area of 30±10 m² g⁻¹) are hydrophobic fumed silica based on Aerosil® OX 50 and Aerosil® 50, respectively, treated with silicone oil. Aerosil® RX 50 (specific surface area of 35±10 m² g⁻¹) and Aerosil® NAX 50 (specific surface area of 40±10 m² g⁻¹) are Aerosil® 50 nanoparticles surface modified with hexamethyldisilazan.

Organically modified clay CLOISITE 30B was obtained from Rockwood Clay Additives. CLOISITE 30B is a natural montmorillonite modified with alkyl quaternary ammonium salts, with 65% of molecules containing alkyl residue with 18 carbon atoms, 30% of the alkyl group with 16 carbon atoms and 5% of molecules containing alkyl groups with 14 carbon atoms. In the dry state, 90% of the clay particles have size below 13 μm. All chemicals were used as received without further purification.

Synthesis of UPe resins

Synthesis of UPe1

PET waste depolymerization was performed by glycolysis with DPG. In a four-necked flask of 250 ml, equipped with a mechanical stirrer, thermometer, condenser and inlet for nitrogen, 57.2 g of PET, 61.8 g of DPG and 0.2 g of TBT were placed (Table 1). The glycolysis reaction lasted for 5 hours at 210 °C, after which the reaction mixture was cooled to 90 °C. The hydroxyl value of the resulting glycolyzate was 315 mg KOH g⁻¹. Then, a Dean-Stark evaporator was added onto the flask and maleic anhydride (38.0 g) and 0.02 g of HQ were added (Table 1). The mixture was heated to 115 °C, providing constant temperature for 1 h, and then the continual temperature increase was achieved at a heating rate of 15 °C h⁻¹. When the reaction mixture temperature reached 150 °C, xylene (3 wt.%) was added to provide continual water removal by binary azeotrope, assuring in this manner a driving force for reaching the end-point of the reaction at 210 °C. After completion of the reaction, the obtained resin was cooled to 120 °C, 0.02 g of hydroquinone dissolved in 0.2 ml of ethanol was added, and then vacuum distillation (water pump) was carefully applied for 1 h to remove low boiling compounds present in the final product. Then, the resin was cooled down to 100 °C and styrene (40 wt.%) was added, followed by mixing to ensure homogeneity of the product (UPe1).

¹H- and ¹³C-NMR data of UPe1 resin

¹H-NMR (CDCl₃): 1.24 (*m*, 12H, O-CH₂-CH(CH₃)-O), 3.58 (*m*, 6H, O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 4.50 (*m*, 6H, O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 5.22 (*d*, 1H, styrene), 5.74 (*d*, 1H, styrene), 6.68 (*q*, 1H, styrene), 6.77 (*m*, 2H, O-(O)C-CH=CH-C(O)-O), 7.31 (*m*, 5H, styrene), 8.08 (*m*, 4H, H_{Ar}).

¹³C-NMR (CDCl₃): 16.5 (O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 18.4 (O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 70.3 (O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 70.7 (O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 73.4 (O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 76.3 (O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 113.7; 126.1; 127.8; 128.3 (styrene), 128.4 (O=C-HC=CH-C=O), 129.6 (C_{Ar}), 133.6 (C_{Ar}), 136.7; 137.4 (C, styrene), 165.4 (O-C(O)-CH=CH-C(O)-C), 174.1 (O-C(O)-Ar-C(O)-O).

Synthesis of UPe2

Depolymerization of PET waste was performed by glycolysis with TEG. In a 250 ml four-necked flask, equipped with a mechanical stirrer, thermometer, condenser and inlet for nitrogen, 61.2 g of PET, 68.8 g of TEG and 0.2 g of TBT were placed (Table 1). The reaction of glycolysis lasted for 5 hours at 210 °C, after which the reaction mixture was cooled to 90 °C. The hydroxyl value of the resulting glycolyzate was 292 mg KOH g⁻¹. Then, a Dean-Stark water separator was assembled on the flask and maleic anhydride (40.4 g) and HQ (0.02 g) were added (Table 1). The synthesis of UPe2 was performed in the same manner as synthesis of UPe1.

¹H- and ¹³C-NMR data for UPe2 resin (Ar is terephthaloyl moiety):

¹H-NMR (CDCl₃): 1.24 (*m*, 12H, O-CH₂-CH(CH₃)-O), 2.43 (*m*, 4H, H-6, H-3, THP), 3.04 (*m*, 2H, H-1, H-2, THP), 3.58 (*m*, 6H, O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 4.50 (*m*, 6H, O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 5.22 (*d*, 1H, styrene), 5.74 (*d*, 1H, styrene), 6.68 (*q*, 1H, styrene), 6.77 (*m*, 2H, O-(O)C-CH=CH-C(O)-O), 7.31 (*m*, 5H, styrene), 8.08 (*m*, 4H, H_{Ar}).

¹³C-NMR (CDCl₃): 16.5 (O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 18.4 (O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 70.3 (O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 70.7 (O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 73.4 (O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 76.3 (O-CH₂-CH(CH₃)-O-CH₂-CH(CH₃)-O), 113.7; 126.1; 127.8; 128.3 (styrene), 128.4 (O=C-HC=CH-C=O), 129.6 (C_{Ar}), 133.6 (C_{Ar}), 136.7; 137.4 (C, styrene), 165.4 (O-C(O)-CH=CH-C(O)-C), 174.1 (O-C(O)-Ar-C(O)-O).

Production of composites based on UPe1 and UPe2 resins

Unsaturated polyester samples, UPe1 and UPe2, were used as the polymer matrix for the production of composite materials with addition of the following fillers: various commercial organically modified SiO₂ nanoparticles (RX50, NAX50, RY50 and NY50), organically modified clay CLOISITE 30B, rutile TiO₂ or GP. The composites (UPeN/filler) based on UPeN (where index N designates UPe resin – Upe1 and UPe2) and selected filler were obtained by mixing (grinding) appropriate amount of filler with UPeN (60 wt.% in styrene), using both modified laboratory homogenizer and ultrasonic bath. The pure UPeN and composites, (UPeN/filler), based on UPeN (60 wt.% in styrene) were cured using benzoyl peroxide (1.0 wt.%) as initiator and *N,N*-dimethylaniline (0.5 wt.%) as an accelerator.

All experiments used for the preparation of composites were conducted in three steps: weighted UPeN and filler components were carefully blended (homogenized) for 30 min using a modified laboratory homogenizer. In the second step, the sticky paste was transferred to an ultrasonic bath and treated under ultrasound for 15 min at 30 °C. The ultrasonic bath (Bandelin electronic, Berlin, Germany, power 120 W, frequency 35 kHz) was thermostated by circulating cold water through the jacket. After the addition of the accelerator and blending in a modified laboratory homogenizer at high speed (800^o/min) for 1 min, the initiator was added, and the obtained uncured composite was then blended at 800 °C/min for 1 min and used for loading in PTFE mould. In this manner, UPeN/filler(n) were obtained, where index (*n*) designates percent of added filler (clay CLOISITE 30B: 0.25, 0.5, 1.0, 2.5, 5 and 10 wt.% and the amount of other fillers was 10 wt.%).

Characterization

The composition of the obtained product of glycolysis and the obtained unsaturated polyesters was determined using NMR and FTIR spectroscopy. ¹H and ¹³C-NMR spectra were recorded on Varian Gemini 200 instrument Spectra at room temperature in deuterated chloroform (CDCl₃). Chemical shifts were expressed in ppm (δ) values relative to TMS (tetramethylsilane) in the ¹H-NMR spectra, and the residual solvent signal in ¹³C-NMR spectra. FTIR spectra were recorded in the transmission mode, using a Bomem MB, series Hartmann & Braun, spectrometer and samples in the form of film or KBr tablet.

Table 1. Experimental conditions for UPe1 and UPe2 synthesis

Sample	PET, g	Glycol, g	Catalyst, g	Anhydride, g	Molar ratio OH/COOH	HQ, g	Styrene, g
UPe1	57.2	DPG (61.8)	TBT (0.2)	MA (38.0)	1.1	0.04	104.83
UPe2	61.2	TEG (68.8)	TBT (0.2)	MA (40.4)	1.1	0.04	113.76

The gel time of the samples was determined from the cure exotherm, measured according to ASTM D2471-99. The acid (*AV*) and hydroxyl (*HV*) values were determined according to ASTM D3644 and ASTM D2849 methods, respectively. The number average molecular weight, M_n , of the synthesized UPe was calculated as:

$$M_n = \frac{2 \times 56100}{AV + HV} \quad (1)$$

Stress-strain curves of cross-linked polyester samples and composite materials were obtained from uniaxial tensile experiments, which were carried out at room temperature by the standard method (ASTM D882). Specimens of the materials were prepared in a standard size, and subjected to testing by the use of Testing Machine, AG-Xplus HS, Shimadzu, Japan. Tensile strength, elongation at break and Young's modulus (tensile modulus) for all samples were determined as the mean of five measurements.

RESULTS AND DISCUSSION

As a starting material for unsaturated polyester resins synthesis, intermediate products obtained by depolymerization of PET waste bottles were used. Glycolysis of PET waste with dipropylene glycol or triethylene glycol in the presence of catalysts tetrabutyl titanate was performed. Hydroxyl value of the products obtained by glycolysis in the presence of DPG was 315 mg KOH g⁻¹, and 292 mg KOH g⁻¹ when TEG was used. Based on the determined hydroxyl values of intermediary products, the number average molecular weight obtained by calculation according to Eq. (1) was 356 g mol⁻¹ in the case of DPG and 384 g mol⁻¹ when TEG was used. *AV*, *HV* and values of M_n of the synthesized UPe1 and UPe2 are given in Table 2.

Table 2. *HV*, *AV* and M_n of the synthesized UPe1 and UPe2

Sample	<i>AV</i> / mg KOH g ⁻¹	<i>HV</i> / mg KOH g ⁻¹	M_n / g mol ⁻¹
UPe1	6.55	62.8	1620
UPe2	17.5	51.5	1630

FTIR spectra of the products of PET glycolysis with DPG and TEG are shown in Figure 1. The broad band at ≈3400 cm⁻¹ originates from the stretching vibration of OH valence bond present in terminal hydroxyl groups. In the FTIR spectrum of the product of glycolysis based on TEG, the band at 2975 cm⁻¹, corresponding to the asymmetric deformation of C–H stretching vibration in the methyl group, was not observed due to the lack of methyl groups in TEG. This band is visible in the spectrum of the product of glycolysis based on DPG. Also, for the same reason there is no band at 1377 cm⁻¹, which originates from the bending vibration of C–H

bonds present in the methyl group. The intense band, observed at ≈1720 cm⁻¹, originates from valence vibration of C=O present in ester group. The absorption bands between 1300 and 1100 cm⁻¹ originate from C–O stretching vibrations, asymmetric and symmetric, respectively, present in ester group of terephthalic acid. The band at 879 cm⁻¹ originates from the deformation vibrations of aromatic C–H out of plane connections. It is characteristic of 1,4-disubstituted benzene ring, which in this case comes from the terephthalic acid moiety.

After the reactions of glycolysis, maleic anhydride at the molar ratio of hydroxyl and carboxyl groups of 1.1, was added in the flask. Figure 1 shows also FTIR spectra of the synthesized unsaturated polyesters UPe1 and UPe2. Comparison with spectra of starting product indicates significant reduction in the intensity of band at 3400 cm⁻¹, which originates from the stretching vibration of OH groups. Also, band at 1078 cm⁻¹, which is derived from the alcoholic C–O stretching deformation vibration, is reduced. At the same time, the appearance of new bands at 1644 and 979 cm⁻¹ can be observed in the FTIR spectrum of UPe1 resin, which correspond to the C=C stretching (skeletal) vibration of benzene ring and out of plane bending vibrations of 1,2-*trans* disubstituted C=CH group, present in maleic acid fragment, respectively. Aromatic C–H stretching vibration, overlapped with vinyl group, appeared in the region 3076–3010 cm⁻¹ in the spectra of the synthesized UPe.

The cure exotherms of UPe1 and UPe2, cross-linked with 1.0 wt.% benzoyl peroxide and 0.5 wt.% *N,N*-dimethylaniline, are presented in Figure 2. According to these results, the maximum curing temperature of UPe1 (88 °C) was quite higher and reached earlier (13 min) than for UPe2 (41 °C after 21 min). Curing reaction of UPe1 is faster than curing reaction of UPe2, due to the better miscibility of polyester resin containing DPG with styrene than the resin containing TEG.

Results of the studies of mechanical properties are shown in Figures 3–7, and the values of tensile strength, σ_p , elongation at break, ε_b , and tensile modulus, *E*, of cured UPe1 and UPe2 resins, as well as of corresponding composites are given in Tables 3 and 4. According to the results it could be noticed that cross-linked sample UPe1 showed greater tensile strength and modulus, and lower elongation at break than the cross-linked sample UPe2 (Figure 3, Tables 3 and 4). The reason for this behavior lies in the different flexibility of polyester chain. In the case of polyester Upe2, based on TGE, the spacing between the double bonds in polyester chains is larger than in the UPe1 polyester chains causing more flexible Upe2 chains. Nanocomposites based on UPe1 and clay have no significantly different mechanical properties, *i.e.*, tensile strength and elongation at break are slightly modified, and tensile modulus decreases with increasing clay content and this

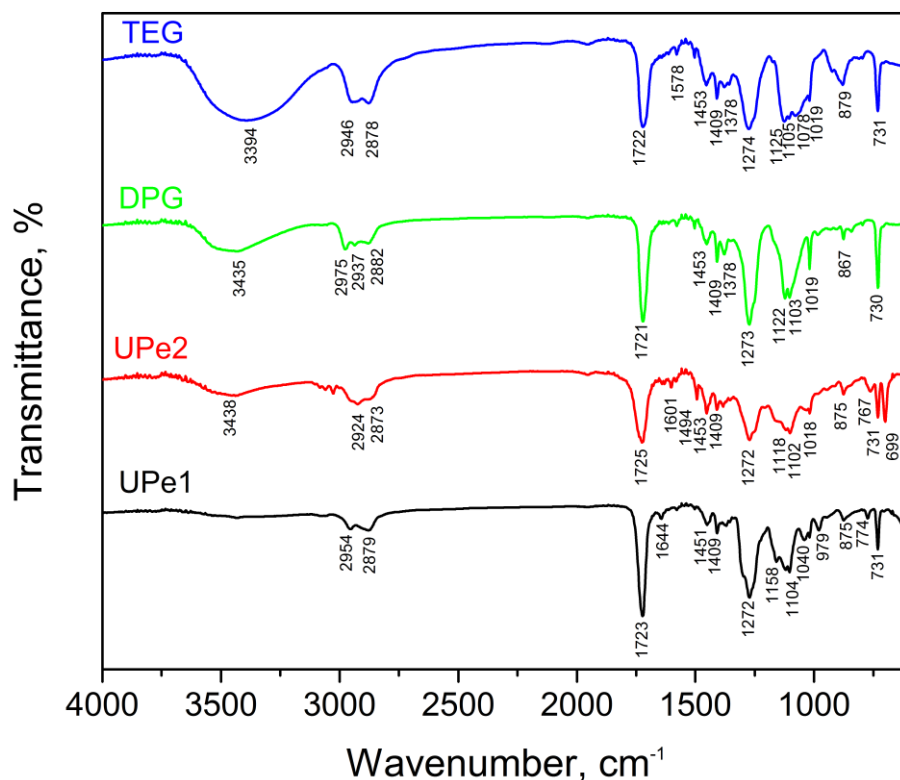


Figure 1. FTIR Spectra of UPe1, UPe2, and glycolyzed products (obtained using DPG and TEG).

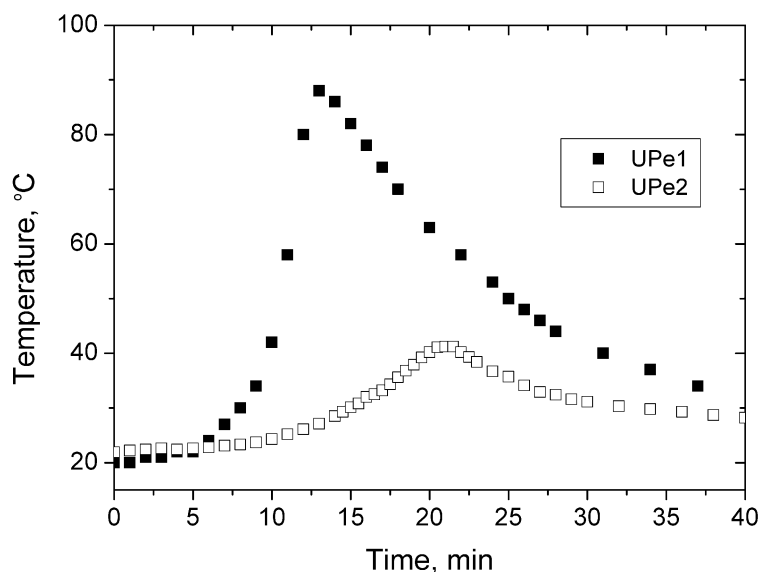


Figure 2. The cure exotherms of UPe1 and UPe2 cross-linked with 1.0 wt.% benzoyl peroxide and 0.5 wt.% *N,N*-dimethylaniline.

change is less than 10% compared to the pure polyester (Figure 4, Table 3).

The greatest influence on the mechanical properties of the composites was found when graphite and TiO₂ (10 wt.%) were added as fillers, which is reflected as significant increase of the tensile modulus, tensile strength and decrease of the elongation at break compared to the corresponding UPe resins (Figure 5, Table 3). In the case of nanocomposites prepared from UPe2

resin, the addition of hydrophobically modified silica nanoparticles leads to decrease of tensile strength and tensile modulus, which indicates a weak interaction between the filler particles and the polymer matrix (Figure 6, Table 4). The largest decrease in tensile strength and tensile modulus was observed in composite samples obtained after addition of nanofiller particles AEROSIL® RY50, due to low intensity of interaction between nanofiller, modified with silicone oil,

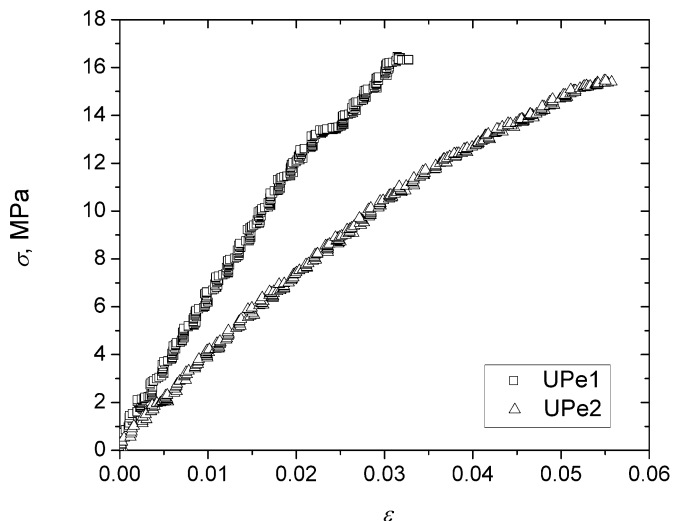


Figure 3. The stress-strain curves of the cured samples UPe1 and UPe2.

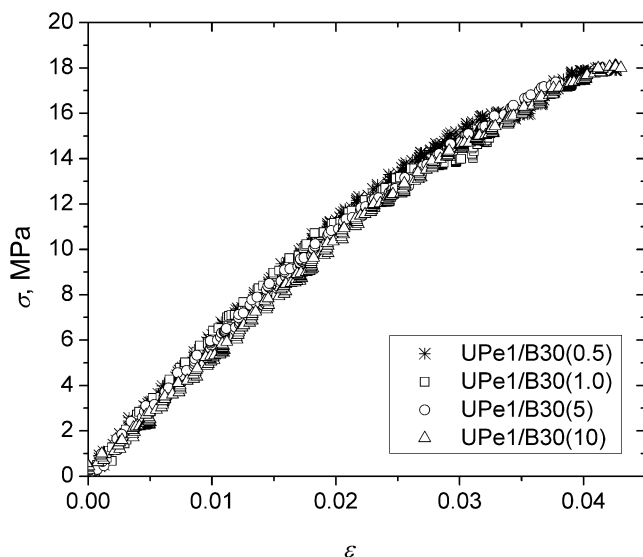


Figure 4. The stress-strain curves of the nanocomposites based on UPe1 and CLOISITE 30B.

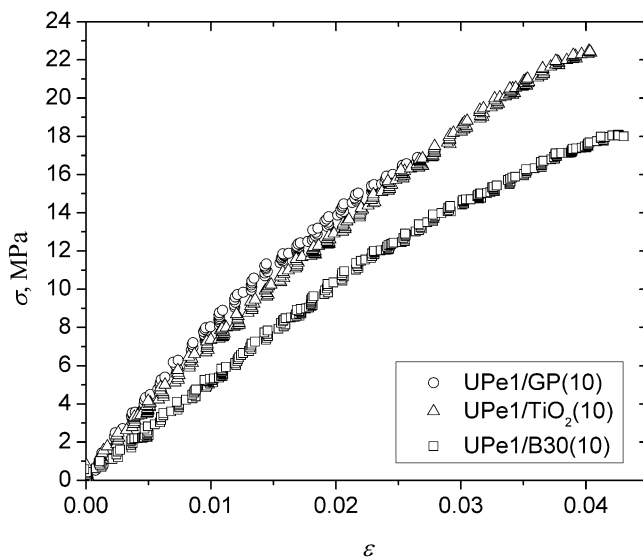


Figure 5. The stress-strain curves of the composites based on UPe1 and graphite, clay and titanium dioxide.

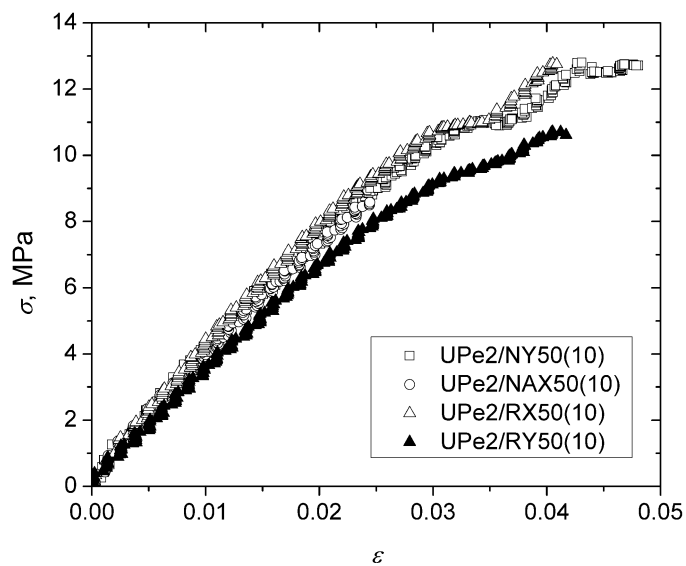


Figure 6. The stress-strain curves of the nanocomposites based on UPe2 and AEROSIL® nanofillers.

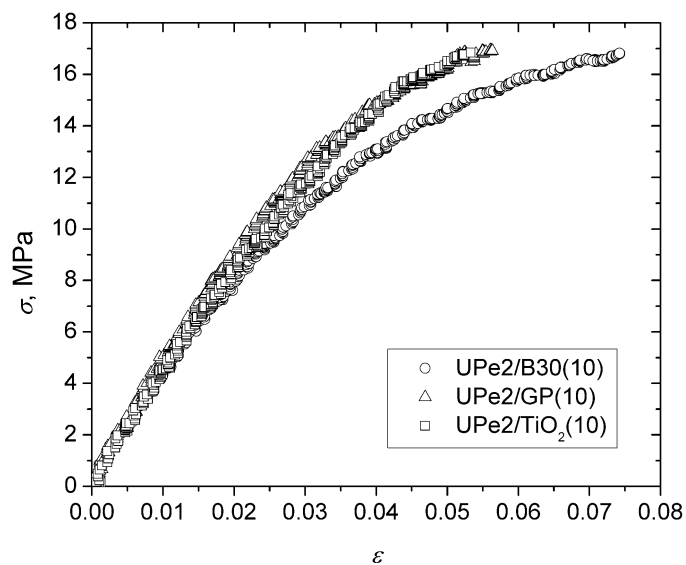


Figure 7. The stress-strain curves of the composites based on UPe2 and graphite, clay and titanium dioxide.

Table 3. Results of the mechanical testing of cured UPe1 and corresponding composites

Sample	σ_p / MPa	ϵ_{max} / %	E / MPa
UPe1	16.33	3.27	647
UPe1/B30(0.25)	15.96	3.44	656
UPe1/B30(0.5)	15.87	3.30	624
UPe1/B30(1.0)	14.92	3.24	606
UPe1/B30(2.5)	19.95	3.68	604
UPe1/B30(5)	17.34	3.78	597
UPe1/B30(10)	18.00	4.30	606
UPe1/GP(10)	16.90	2.65	805
UPe1/TiO ₂ (10)	22.45	4.03	741

Table 4. Results of mechanical testing of cured UPe2 and corresponding composites

Sample	σ_p / MPa	ε_{max} / %	E / MPa
UPe2	15.22	5.66	421
UPe2/NY50(10)	11.08	3.55	422
UPe2/NAX50(10)	14.83	6.00	408
UPe2/RX50(10)	12.79	4.39	446
UPe2/RY50(10)	10.62	4.17	363
UPe2/GP(10)	16.91	5.64	510
UPe2/B30(10)	16.82	7.42	457
UPe2/TiO ₂ (10)	16.57	5.36	454

and cross-linked UPe2 resin. The presence of 10 wt.% clay, graphite or TiO₂ in UPe2 resin increased tensile strength and tensile modulus, which indicates stronger interaction between filler particles themselves and matrix and filler particles (Figure 7, Table 4).

CONCLUSION

Maleic anhydride and di-hydroxyl functional products obtained after catalytic glycolysis of PET waste, using dipropylene glycol or triethylene glycol, were used for the synthesis of unsaturated polyesters. The glycolized products and UPe resins were characterized by FTIR spectroscopy, acid and hydroxyl value. Curing reaction of UPe1 was faster than curing reaction of UPe2 due to the better miscibility of styrene with polyester resin based on glycolized product which contains DPG. Due to the higher polymer chain rigidity, UPe1 showed higher tensile strength and modulus, and lower elongation at break than UPe2.

The obtained UPe resins were further used as matrix for the synthesis of composites using chemically modified silica nanoparticles or clay CLOISITE 30B, as well as graphite powder or TiO₂ as fillers. The influence of reinforcing agents on the mechanical properties of the prepared composites was investigated. It was shown that the addition of CLOISITE 30B to the UPe1 had no significant influence on the mechanical properties, while tensile strength and tensile modulus of UPe2 increased after adding 10 wt.% of clay. The greatest influence on the mechanical properties of the composites was found when graphite and TiO₂ (10 wt.%) were added as fillers to the synthesized UPe, which is reflected as significant increase of tensile modulus, tensile strength and decrease of the elongation at break, indicating strong interaction between matrix and filler particles. On the other hand, tensile strength and tensile modulus of nanocomposites prepared from UPe2 resin and hydrophobically modified silica nanoparticles decreased, while the composite prepared with AEROSIL® RY50 had the lowest mechanical properties.

Acknowledgement

The authors acknowledge financial support from Ministry of Education, Science and Technological development of Serbia, Project No. 172013.

REFERENCES

- [1] S.M. Al-Salem, P. Lettieri, J. Baeyens, Recycling and recovery routes of plastic solid waste (PSW): a review, *Waste Manag.* **29** (2009) 2625–2643.
- [2] R. López-Fonseca, I. Duque-Ingunza, B. de Rivas, L. Flores-Giraldo, J.I. Gutiérrez-Ortiz, Kinetics of catalytic glycolysis of PET wastes with sodium carbonate, *Chem. Eng. J.* **168** (2011) 312–320.
- [3] K. Li, X. Song, D. Zhang, Depolymerization of poly(ethylene terephthalate) with catalyst under microwave radiation, *J. Appl. Polym. Sci.* **109** (2008) 1298–1301.
- [4] R. López-Fonseca, M.P. González-Velasco, J.R. González-Velasco, J.I. Gutiérrez-Ortiz, A kinetic study of the depolymerisation of poly(ethylene terephthalate) by phase transfer catalysed alkaline hydrolysis, *J. Chem. Technol. Biotechnol.* **84** (2009) 92–99.
- [5] M. Goto, H. Koyamoto, A. Kodama, T. Hirose, S. Nagao, B.J. McCoy, Degradation kinetics of polyethylene terephthalate in supercritical methanol, *AIChE J.* **48** (2002) 136–144.
- [6] M.E. Tawfik, S.B. Eskander, Chemical recycling of poly(ethylene terephthalate) waste using ethanolamine, Sorting of the end products, *Polym. Degrad. Stab.* **95** (2010) 187–194.
- [7] F. Pardal, G. Tersac, Kinetics of poly(terephthalate) glycolysis by diethylene glycol. I. Evolution of liquid and solid phases, *Polym. Degrad. Stab.* **91** (2006) 2840–2847.
- [8] C.-H. Chen, C.-Y. Chen, Y.-W. Lo, C.-F. Mao, W.-T. Liao, Studies of glycolysis of poly(ethylene terephthalate) recycled from postconsumer soft-drink bottles. I. Influences of glycolysis conditions, *J. Appl. Polym. Sci.* **80** (2001) 943–948.
- [9] R. López-Fonseca, I. Duque-Ingunza, B. de Rivas, S. Arnaiz, J.I. Gutiérrez-Ortiz, Chemical recycling of post-consumer PET wastes by glycolysis in the presence of metal salts, *Polym. Degrad. Stab.* **95** (2010) 1022–1028.
- [10] G.P. Karayannidis, D.S. Achilias, I.D. Sideridou, D.N. Bikiaris, Alkyd resins derived from glycolized waste poly-

- (ethylene terephthalate), *Eur. Polym. J.* **41** (2005) 201–210.
- [11] A. Torlakoglu, G. Güçlü, Alkyd–amino resins based on waste PET for coating applications, *Waste Manag.* **29** (2009) 350–354.
- [12] M. Kathalewar, N. Dhoptkar, B. Pacharane, A. Sabnis, P. Raut, V. Bhave, Chemical recycling of PET using neopentyl glycol: Reaction kinetics and preparation of polyurethane coatings, *Prog. Org. Coat.* **76** (2013) 147–156.
- [13] G. Güçlü, M. Orba, Alkyd resins synthesized from post-consumer PET bottles, *Prog. Org. Coat.* **65** (2009) 362–365.
- [14] D.J. Suh, O.O. Park, K.H. Yoon, The properties of unsaturated polyester based on the glycolized poly(ethylene terephthalate) with various glycol compositions, *Polymer* **41** (2000) 461–466.
- [15] J.M.L. Reis, Effect of aging on the fracture mechanics of unsaturated polyester based on recycled PET polymer concrete, *Mat. Sci. Eng., A* **528** (2011) 3007–3009.
- [16] A.M. Atta, M.E. Abdel-Raouf, S.M. Elsaheed, A.-A.A. Abdel-Azim, Curable resins based on recycled poly(ethylene terephthalate) for coating applications, *Prog. Org. Coat.* **55** (2006) 50–59.
- [17] Cs. Varga, N. Miskolczi, L. Bartha, G. Lipóczy, Improving the mechanical properties of glass-fibre-reinforced polyester composites by modification of fibre surface, *Mater. Design* **31** (2010) 185–193.
- [18] R. Sengupta, M. Bhattacharya, S. Bandyopadhyay, A.K. Bhowmick, A review on the mechanical and electrical properties of graphite and modified graphite reinforced polymer composites, *Prog. Polym. Sci.* **36** (2011) 638–670.
- [19] S.S. Ray, M. Okamoto, Polymer/layered silicate nanocomposites: a review from preparation to processing, *Prog. Polym. Sci.* **28** (2003) 1539–1641.
- [20] M. Zhang, R.P. Singh, Mechanical reinforcement of unsaturated polyester by Al₂O₃ nanoparticles, *Mat. Lett.* **58** (2004) 408–412.
- [21] L. Tibiletti, C. Longuet, L. Ferry, P. Coutelen, A. Mas, J.-J. Robin, J.-M. Lopez-Cuesta, Thermal degradation and fire behaviour of unsaturated polyesters filled with metallic oxides, *Polym. Degrad. Stab.* **96** (2011) 67–75.
- [22] Y.-F. Shih, Y.-T. Wang, R.-J. Jeng, K.-M. Wei, Expandable graphite systems for phosphorus-containing unsaturated polyesters. I. Enhanced thermal properties and flame retardancy, *Polym. Degrad. Stab.* **86** (2004) 339–348.
- [23] L.B. Manfredi, E.S. Rodríguez, M. Wladyka-Przybylak, A. Vázquez, Thermal degradation and fire resistance of unsaturated polyester, modified acrylic resins and their composites with natural fibres, *Polym. Degrad. Stab.* **91** (2006) 255–261.
- [24] K.A. Carrado, in G.A. Shonaike, S.G. Advani, (Eds.), *Advanced Polymeric Materials: Structure Property Relationships*, CRC Press, Boca Raton, FL, 2003, Ch. 10.
- [25] X. Kornmann, L.A. Berglund, J. Sterte, E.P. Giannelis, Nanocomposites based on montmorillonite and unsaturated polyester, *Polym. Eng. Sci.* **38** (1998) 1351–1358.
- [26] R.K. Bharadwaj, A.R. Mehrabi, C. Hamilton, C. Trujillo, M. Murga, R. Fan, A. Chavira, A.K. Thompson, Structure–property relationships in cross-linked polyester–clay nanocomposites, *Polymer* **43** (2002) 3699–3705.
- [27] M. Chieruzzi, A. Miliuzzi, J.M. Kenny, Effects of the nanoparticles on the thermal expansion and mechanical properties of unsaturated polyester/clay nanocomposites, *Composites, A* **45** (2013) 44–48.
- [28] P. Jawahar, R. Gnanamoorthy, M. Balasubramanian, Tribological behaviour of the clay-thermoset nanocomposites, *Wear* **261** (2006) 835–840.
- [29] P. Kiliaris, C.D. Papaspyrides, Polymer/layered silicate (clay) nanocomposites: An overview of flame retardancy, *Prog. Polym. Sci.* **35** (2010) 902–958.
- [30] J.C. Huang, Zk Zhu, J. Yin, X.f. Qian, Y.Y. Sun, Poly(etherimide)/montmorillonite nanocomposites prepared by melt intercalation: morphology, solvent resistance properties and thermal properties, *Polymer* **42** (2001) 873–877.
- [31] B.-W. Jo, S.-K. Park, D.-K. Kim, Mechanical properties of nano-MMT reinforced polymer composite and polymer concrete, *Constr. Build. Mater.* **22** (2008) 14–20.
- [32] S. Katoch, V. Sharma, P.P. Kundu, Water sorption and diffusion through saturated polyester and their nanocomposites synthesized from glycolized PET waste with varied composition, *Chem. Eng. Sci.* **65** (2010) 4378–4387.

IZVOD

MEHANIČKA SVOJSTVA KOMPOZITA NA BAZI NEZASIĆENIH POLIESTARSKIH SMOLA DOBIJENIH HEMIJSKOM RECIKLAŽOM POLI(ETILEN-TEREFTALATA)

Aleksandar D. Marinković¹, Tijana Radoman², Enis S. Džunuzović¹, Jasna V. Džunuzović³, Pavle Spasojević¹, Bojana Isailović¹, Branko Bugarski¹

¹*Tehnološko–metalurški fakultet, Univerzitet u Beogradu, Beograd, Srbija*

²*Inovacioni centar, Tehnološko–metalurški fakultet, Univerzitet u Beogradu, Beograd, Srbija*

³*IHTM – Centar za Hemiju, Univerzitet u Beogradu, Beograd, Srbija*

(Naučni rad)

U ovom radu sintetisani su kompoziti na bazi nezasićenih poliestarskih (UPe) smola i SiO₂ (AEROSIL®:RY 50, NY 50, RX 50 i NAX 50), grafita, TiO₂ ili organski modifikovane gline CLOISITE 30B u cilju ispitivanja uticaja punioca na mehanička svojstva kompozita. Nezasićene poliestarske smole su sintetisane polazeći od anhidrida maleinske kiseline i proizvoda glikolize dobijenih depolimerizacijom poli(etilen-tereftalata) sa dipropilen glikolom (UPe1 smola) ili trietilen glikolom (UPe2 smola) u prisustvu katalizatora tetrabutil titanata. Sintetisane nezasićene poliestarske smole su ispitane primenom FTIR spektroskopije, određen im je kiselinski i hidroksilni broj i ispitana su njihova mehanička svojstva. Molarna masa srednja po brojnoj vrednosti sintetisanih nezasićenih poliestarskih smola je između 1620–1630 g mol⁻¹. Moduli istezanja i zatezna čvrstoća kompozita pripremljenih dodavanjem 10 mas.% grafita ili TiO₂ nezasićenim poliestarskim smolama su značajno porasli u odnosu na čiste poliestre, dok se izduženje pri kidanju smanjilo, što ukazuje na postojanje jakih interakcija između matrice i čestica punioca. Sa druge strane, nanokompoziti sintetisani korišćenjem UPe2 i modifikovanih nanočestica SiO₂ su imali manju zateznu čvrstoću i module istezanja nego čista nezasićena poliestarska smola. Pokazano je da prisustvo gline CLOISITE 30B nema značajan uticaj na mehanička svojstva smole UPe1, dok su vrednosti modula istezanja i zatezne čvrstoće UPe2 porasle nakon dodavanja 10 mas.% gline.

Ključne reči: Poli(etilen-tereftalat) • Hemijska reciklaža • Kompoziti • Mehanička svojstva